

GB935425

1, 3–butadiene/isoprene copolymers

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Abstract of **GB935425**

Linear copolymers of 1,3–butadiene and isoprene containing up to 90% of isoprene and wherein at least 70% of the diene units are cis–1,4 are prepared by polymerizing, in an aromatic solvent, a monomer mixture having a composition equal to that desired in the copolymer, the polymerization being in the presence of a soluble catalyst obtained from an aluminium dialkyl monohalide and a cobalt complex and the reaction mixture consisting of pure monomers with/without inert components such as inert gases (e.g. nitrogen) or aliphatic or non–polymerizable olefinic hydrocarbons. The catalyst may be obtained from cobalt acetylacetonate or cobaltous chloridepyridine complexes, and dialkyl aluminium chloride, and may be prepared in the presence of monomer. Specified aromatic solvents are toluene, benzene and halogenated benzenes. In examples methanol and hydrochloric acid are used in working up the product. Specification 916,000 is referred to.



PATENT SPECIFICATION

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COMPLETE SPECIFICATION

1,3-Butadiene/Isoprene Copolymers

We, MONTECATINI SOCIETA GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA, a Body Corporate organised and existing under the laws of Italy, of 18 Via Filippo Turati, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

10 This invention relates to 1,3-butadiene/isoprene copolymers.

The use of soluble catalysts, obtained from $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and cobalt complexes, for preparing butadiene polymers having substantially *cis*-1,4 structure has been described in earlier Patent Specifications such as 916,000. These catalysts can also be used to polymerise conjugated diolefins other than butadiene, e.g. isoprene. It has however been found that from isoprene, at least under ordinary conditions, polymers very rich in *cis*-1,4 units are not obtained as would be the case of butadiene; the polyisoprenes obtained at room temperature are generally found to consist of macromolecules having 1,4-units (about 55%) and 3,4 units (about 45%).

Moreover the rate of polymerisation of isoprene with these catalysts is tens of times lower than that of butadiene, at the same temperature.

It is possible with the aid of the aforementioned catalysts to prepare copolymers of butadiene with isoprene. However, it has not been possible to obtain copolymers containing high proportions of isoprene in the macromolecule; in the copolymers obtained up till now which contain up to about 10% isoprene, the isoprene units had various structures, for example primarily *cis*-1,4 and 3,4 structures.

We have found (and this is a first feature of this invention) that, by using monomers free from acetylenic and allenic hydrocarbons and from sulphur compounds, i.e. by starting from practically pure monomers or from a feed containing, in addition to the monomers, only

components which are inert to the catalyst, such as saturated aliphatic hydrocarbons or olefin hydrocarbons not polymerisable by the catalysts in question or nitrogen or other inert gases, and carrying out the polymerisation in the presence of aromatic solvents, the copolymerisation can lead to copolymers having the desired composition.

It is known that when two monomers are copolymerised, they do not enter into the copolymer in the same molar ratios as those existing in the feed mixture; this is as a rule particularly so in cases such as the one under consideration, in which the polymerisation rates of the two monomers are very different from each other. In other words, if we indicate with $d[M_1]$ and $d[M_2]$ the mols of the two monomers copolymerised in an infinitesimal time interval, wherein $[M_1]$ and $[M_2]$ are the concentrations of the unreacted monomers, the position usually is that

$$\frac{d[M_1]}{d[M_2]} \text{ is different from } \frac{[M_1]}{[M_2]}$$

For this reason, when starting from a given mixture of the two monomers, the composition of the monomer mixture varies during the copolymerisation and therefore also the composition of the copolymers obtained varies with time.

Except in very rare cases, such as, azeotropic polymerisation copolymers having a constant composition can be prepared only by keeping constant during polymerisation the concentration of both monomers: this can be obtained by continuously restoring the feed composition as the polymerisation proceeds or by taking various technical precautions which however render the process difficult.

We have now found that, with certain catalysts and starting from very pure monomers as stated hereinbefore, copolymerisation of butadiene with isoprene can be carried out

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so that the ratio between the polymerisation rates of the two monomers is practically the same as the ratio between their concentration. Under such conditions the two monomers are copolymerised in the same molar ratios as those of the feed mixture; that is to say that in each instant

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}$$

This makes it possible to eliminate, with an obvious practical advantage, the precautions which previously had to be followed when the two monomers to be copolymerised, had different copolymerisation rates.

It is known to those skilled in the art that, to represent the course of a copolymerisation, the reactivity coefficients of the two monomers, usually indicated by r_1 and r_2 , are introduced (for their definition see J. P. Flory—Principles of Polymer Chemistry—1953, page 179 *et. seq.*). In the most common polymerisation r_1 is usually different from r_2 and the r_1/r_2 ratio is in general of the same order as that of the v_1/v_2 ratio between the homopolymerisation rates; in the copolymerisation of isoprene and butadiene under the conditions found by us, it happens that $r_1 = r_2 = 1$, though v_1 (isoprene homopolymerisation rate) is some tens of times lower than v_2 (butadiene homopolymerisation rate). This type of copolymerisation therefore represents a particular case which could not be foreseen from what was known from the homopolymerisation of the two monomers.

The invention provides high molecular weight linear copolymers of 1,3-butadiene and isoprene which copolymers contain up to 90% of units of copolymerised isoprene and in which at least 70% of the total diene units present have *cis*-1,4 structure.

The invention further provides a process for preparing copolymers according to the invention wherein a monomer mixture having a composition by weight equal to that desired for the copolymer is copolymerised in an aromatic solvent, in the presence of a hydrocarbon soluble catalyst obtained from an aluminium dialkyl monohalide and a cobalt complex, said mixture consisting only of the two pure monomers or containing, in addition to the monomers, only components inert to the catalyst.

In the Examples given hereinafter copolymerisation runs are reported which illustrate what has been stated above. The composition of the feed mixture was varied in the various runs over a remarkably wide range, i.e. from about 3% to about 90% isoprene.

During the copolymerisation various samples of the formed copolymer were withdrawn at different times and analysed by infra-red spectroscopy. The results obtained from the

analysis of the copolymer withdrawn after successive time intervals from the beginning of the copolymerisation are practically equal to each other and show that the copolymer has a composition very similar (within the limits of error of infra-red analysis) to that of the feed mixture.

In order to prepare a copolymer having a given composition it is therefore sufficient to introduce into the copolymerisation reactor the two monomers in the same ratio as that desired for the copolymer.

We have already observed that, while butadiene homopolymers obtained with the aid of the catalyst used here have a substantially *cis*-1,4 structure (>95%), isoprene homopolymers obtained with the same catalysts have a mixed 1,4- and 3,4-structure and the isoprene units contained in the copolymers obtained up till now have various structures, without a clear prevalence of one of them over the other.

Surprisingly, in the copolymers obtained according to the present invention the copolymerised isoprene units have prevailingly *cis*-1,4 structure, the 3,4 units being present in an amount much lower than that found in homopolymers produced with the same catalysts or in the previously known copolymers. This represents a further confirmation that the products obtained are real copolymers and not mechanical mixtures of the two homopolymers.

In the copolymers containing low proportions of isoprene units (<10%), at least 95% of these units have *cis*-1,4 configuration; in the copolymers containing higher proportions of isoprene units (60—70%) a slight increase in the proportion of 3,4 isoprene units is noted but the *cis*-1,4 units remain always prevailing (at least about 80% of the total isoprene units).

It is known that in elastomers obtained from diolefin polymers the dynamic properties (rebound elasticity, hysteresis, etc.) also depend on the configuration of the monomeric units and that these properties are better when the monomeric units have 1,4-configuration instead of 1,2- or 3,4-. The practical interest of what has been stated above concerning the composition of the products obtained in accordance with the invention is therefore clear.

The characteristics of the butadiene/isoprene copolymers prepared according to the present invention vary by varying their percent composition. Copolymers containing low proportions of isoprene units (3—4%) have a melting point slightly lower than that of polybutadiene, but are still capable of crystallising under stretch at room temperature. By increasing the isoprene content, the melting point of the copolymer is lowered and elastomers which do not crystallise under stretch are obtained. By varying the isoprene content it is therefore possible to obtain products of

remarkably different properties, suitable for various uses.

5 An interesting feature of the butadiene/isoprene copolymers consists in the fact that some characteristics are better than those of the polymers obtained from butadiene alone. It is known in fact that polybutadienes rich in *cis*-1,4 units have very good elastic and mechanical properties; however they have poor adhesion and a tear strength lower than that of natural rubber.

It has now been found that these latter properties are improved in the copolymers obtained according to the present invention.

15 The polymerisation catalyst may be prepared according to the methods already described for example in Patent Specification 916,000, i.e. by reacting (usually in an aromatic solvent) a cobalt complex (e.g. the acetylacetonate or complexes of the cobaltous chloride/pyridine type) with $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$.

20 The catalyst can be prepared in the presence of one or both monomers. The aromatic solvent may for example be toluene, benzene or a halogenated benzene derivative such as chlorobenzene.

25 The polymerisation temperature can be varied within wide limits, i.e. between 100° and -80°C , preferably between 50 and -50°C . The practical operating method is not different from that described for the homopolymerisation of butadiene and is illustrated in the following Examples in which all percentages are by weight and the operating conditions are in accordance with the invention.

35 The invention includes elastomers and vulcanized articles consisting of or containing copolymers according to the invention.

EXAMPLE 1

40 Copolymerisation can be carried out under the aforementioned conditions, details are given in Table 1. As a specific example the

copolymerisation according to run 3 is described.

An 0.5 litre glass reactor is used, provided with an agitator and dropping funnel, in which air has been replaced by anhydrous nitrogen. 45

The following substances are placed in the reactor:

140 cc	toluene	50
19.6 g	butadiene	
23.2 g	isoprene	
1 cc	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	

and the following substances in the dropping funnel: 55

65 cc	toluene
1 cc	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$
0.0045 g	cobalt diacetylacetonate.

After 20 minutes the catalyst solution is introduced from the dropping funnel into the reactor (kept at a constant temperature of 13°C) thus starting the copolymerisation. 60

90 minutes after the start a sample of the polymerisation solution is withdrawn from the reactor, the polymer therein contained is coagulated with methanol and hydrochloric acid, washed with pure methanol, vacuum dried at room temperature and finally subjected to infra-red examination. 65

The analysis shows that 54% isoprene is present in the copolymer. Similar samples withdrawn after 175, 245, 360 and 425 minutes from the beginning of the polymerisation, show that the copolymer composition does not alter with time. 70 75

The other runs of the table were carried out in the same way only the feed composition or the catalyst being varied.

In Table 2 are reported the results of the infra-red examination of the copolymers obtained in some of the runs listed in Table 1. 80

TABLE 1
Butadiene-isoprene copolymerization

Run	Co g × 10 ⁻³	Al(C ₂ H ₅) ₂ Cl cc	toluene cc	feed isoprene		T °C.	withdrawals of samples										final conver- sion %
				g	% by weight on the sum of both monomers		1st		2nd		3rd		4th		5th		
							time min.	iso- prene % by weight	time min.	iso- prene % by weight	time min.	iso- prene % by weight	time min.	iso- prene % by weight	time min.	iso- prene % by weight	
1	0.6	1	60	7	90	-15	7200	90.2	—	—	—	—	—	—	—	—	30
2	4	5	250	28.6	74	0	60	73	240	74	—	—	—	—	—	—	26
3	1	2	205	23.2	54	13	90	54	175	52	245	53	360	54	425	53	26
4	1	2	215	23	46	13	60	46	80	48	120	48	150	47	180	47	17
5	3	3	205	13.6	31	0	60	30	120	30	150	29	180	30	240	29	42
6	1	2	250	4.8	10	0	31	7	140	7	—	—	—	—	—	—	28
6 a	9	10	600	1.5	3	0	60	3.2	—	—	—	—	—	—	—	—	50
7 (+)	0.3	1	40	4	50	48	10	50	—	—	—	—	—	—	—	—	50
8 (++)	0.8	4	60	5.3	55	20	45	55	—	—	—	—	—	—	—	—	50

(+) The catalyst was prepared in the presence of butadiene.

(++) The catalyst was prepared from cobalt chloride-pyridine in the presence of butadiene.

In all other runs Co-diacetylacetonate was used.

TABLE 2

Analysis of the butadiene/isoprene copolymers

Run	Analysis of the copolymer					
	isoprene			butadiene		
	<i>cis</i> -1,4 %	<i>trans</i> -1,4 %	3,4 %	<i>cis</i> -1,4 %	<i>trans</i> -1,4 %	1,2 %
1	68.7	2.9	18.8	5.0	0.1	4.5
2	60.1	—	13.3	13.3	0.5	12.8
4	42.3	—	3.8	39.5	1.0	13.4
6 a	3	—	—	91	2	4
7	40.6	0.5	8.9	44.1	—	5.9
8	46	0.5	9.0	41.5	—	3

EXAMPLE 2

Operating as in Example 1, the following substances were placed in the reaction vessel:

5	140 cc	benzene
	23 g	butadiene
	32 g	isoprene
	0.5 cc	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$

and in the dropping funnel:

10	60 cc	benzene
	0.5 cc	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$
	0.005 g	Co diacetylacetonate

After 20 minutes the catalyst solution is introduced from the funnel into the reaction vessel where the temperature is maintained at 5°C.

After 30 minutes (2.5% conversion), 90 minutes (7.5% conversion) and 12 hours (45% conversion) three samples of the solution are extracted; they are purified and analysed by infra-red spectography as described in Example 1.

In all cases the copolymer composition differs only slightly from that of the original monomer mixture.

EXAMPLE 3

The process is carried out as in the preceding Examples, employing:

30	250 cc	chlorobenzene
	17.5 g	butadiene
	22.7 g	isoprene
	1 cc	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$
	and in the funnel:	

60 cc
1 cc
0.0042 g

chlorobenzene
 $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$
Co diacetylacetonate

The catalyst solution is introduced into the reaction vessel, kept at 0°C, after 20 minutes. Samples of the solution are taken after 15 minutes (5% conversion) and 90 minutes (20% conversion); after purification infra-red analysis shows that the copolymers obtained have the same composition as the starting monomer mixture.

WHAT WE CLAIM IS:—

1. High molecular weight linear copolymers of 1,3-butadiene and isoprene which contain up to 90% of units of copolymerised isoprene and in which at least 70% of the total diene units present have *cis*-1,4 structure.

2. A process for preparing copolymers according to claim 1 wherein a monomer mixture having a composition by weight equal to that desired for the copolymer is copolymerised in an aromatic solvent in the presence of a hydrocarbon soluble catalyst compound as obtained from an aluminium dialkyl monohalide and a cobalt complex said mixture consisting only of the two pure monomers or containing, in addition to the monomers, only components inert to the catalyst.

3. A process according to Claim 2, wherein said additional inert components comprise nitrogen or other inert gases or saturated aliphatic or olefinic hydrocarbons which are not polymerisable by the soluble catalysts employed for the copolymerisation.

4. A process according to Claim 2 or Claim 3, wherein a catalyst obtained from cobalt acetylacetonate or cobaltous chloride-pyridine

complexes, and dialkyl aluminium chloride is used.

- 5 5. A process according to any of Claims 2 to 4, wherein polymerisation is carried out at a temperature of from $+50$ to -50°C .

6. A process according to any one of Claims 2 to 5, wherein the aromatic solvent is toluene.

- 10 7. A process according to any one of Claims 2 to 5, wherein the solvent is benzene or a halogenated benzene derivative.

8. A process for preparing copolymers of 1,3-butadiene and isoprene substantially as

herein described with reference to the foregoing Examples.

9. Copolymers of 1,3-butadiene and isoprene 15 when prepared by the process claimed in any of Claims 2 to 8.

10. Elastomers and vulcanised articles consisting of or containing copolymers of 1,3-butadiene and isoprene as claimed in Claim 1 20 or Claim 9.

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